AN INTER-LABORATORY STUDY OF ASBESTIFORM MINERAL FIBRE LEVELS IN THE WATER SUPPLY OF THUNDER BAY, ONTARIO

September, 1975

Ontario

Ministry of the Environment

The Honourable
William G. Newman,
Minister

Everett Biggs,
Deputy Minister

AN INTER-LABORATORY STUDY OF ASBESTIFORM MINERAL FIBRE LEVELS IN THE WATER SUPPLY OF THUNDER BAY, ONTARIO

September, 1975

ACKNOWLEDGEMENTS

The Ministry gratefully acknowledges the contributions of Dr. R. W. Durham, of the Canada Centre for Inland Waters, Dr. E. J. Chatfield, of the Ontario Research Foundation and Dr. J. R. Kramer of McMaster University, in carrying out the asbestiform fibre analyses and in commenting upon the findings of the inter-laboratory study.

C O N T E N T S

ABSTRACT

An inter-laboratory study of the asbestiform mineral fibre levels in the water supply of Thunder Bay, Ontario, was carried out by the Ontario Ministry of the Environment. The data generated by the laboratories was used to ascertain the range of values obtainable on identical samples, and to pinpoint possible causes of the variations in analytical results.

The mean total asbestiform fibre level reported by the laboratories varied as follows: 0.06, 0.63 and 8.45 million fibres per litre. The actual value of the total fibre concentration in the identical samples can only be considered to lie within the approximate range of these mean values. The grid counting technique employed in the analysis was observed to contribute approximately one order of magnitude to between-laboratory differences. The results also revealed that the laboratories did not agree on the types of fibre present in the samples.

Because of the shortcomings in methodology revealed by this and other studies, it is recommended that an expert committee be established to develop standard definitions of asbestiform mineral fibres, and to provide standard procedures for asbestiform fibre analysis.

AN INTER-LABORATORY STUDY OF ASBESTIFORM MINERAL FIBRE LEVELS IN THE WATER SUPPLY OF THUNDER BAY, ONTARIO

INTRODUCTION

In recent analyses of samples taken from the water supply of Thunder Bay, Ontario, widely varying asbestiform mineral concentrations were reported by different laboratories. In order to establish a consensus concerning the asbestiform fibre concentration of the Thunder Bay water supply, the Ontario Ministry of the Environment initiated an inter-laboratory analytical study. Several Ontario laboratories engaged in the determination of asbestiform minerals were asked to participate.

Guidelines (Appendix A) for the inter-laboratory study were prepared with the following objectives:

(a) *to determine the asbestiform fibre concentration of the Thunder Bay water supply.*

(b) *to ascertain the range of values obtainable from the analysis of identical samples by the participating laboratories.*

(c) *to comment on the probable cause of variabilities in results within and between laboratories.*

This report presents a description of the sampling procedure, the analytical techniques used by the participating laboratories, data summaries and evaluations and comments on the study findings.

PARTICIPATING LABORATORIES

The following Ontario laboratories having expertise in asbestos fibre analysis were invited to participate:

(1) The Ontario Research Foundation, Sheridan Park, Mississauga.

(2) McMaster University, Hamilton.

(3) The Canada Centre for Inland Waters, Burlington.

(4) The Department of National Health and Welfare, Ottawa.

(5) Lakehead University, Thunder Bay.

Owing to the absence of technical staff during the period projected for the study, the last two laboratories mentioned were unable to take part.

EXPERIMENTAL DESIGN

The Ministry study guidelines, formulated in cooperation with the participating laboratories, were designed to provide information on the fibre concentration of the Thunder Bay water supply, and to enable an evaluation to be made of the influence of the following factors on the results:

(1) Sampling

- manner of taking the sample
- weather conditions prevailing during the sampling period

(2) Analytical Procedure

- within - and between - laboratory precision
- laboratory contamination

(3) Interpretation of Observations and Measurements

- definition of asbestiform fibre
- methods of calculation
- statistical procedure

SAMPLING LOCATION AND PROCEDURE

The Bare Point pumping station, which supplies unfiltered water to part of the city of Thunder Bay, was selected as the sampling site. The water supply intake to the station is located 2,400 feet from the shoreline and 6 feet above the bottom of the lake. The samples were taken from a bleed line at a point located just before the water enters the distribution system.

The sampling was conducted in two phases. The first set of samples was collected on May 5th, 1975, during an off-shore wind of 5 m.p.h. After this set had been analyzed, a meeting was held among the analysts and Ministry personnel to discuss the sampling procedure and it was decided to proceed with the second sampling phase in a similar manner to the first. The second set of samples was collected on June 6th, 1975, during an on-shore wind of 11 m.p.h.

Eight 10-litre plastic containers were used to collect each set of samples. The containers were first rinsed and then filled with water from the bleed line over a period of 90 minutes. The containers were numbered 1 to 8 for the first set, and 9 to 16 for the second set, according to the sequence of sampling. Two of the numbers were randomly assigned to each laboratory. At the site, the water in each 10-litre plastic container was used to rinse and fill a pair of 1-litre plastic bottles. Two of these pairs served as the samples for each laboratory. The samples were transported to Toronto on the same day the sampling took place and distributed to the laboratories on the following day.

METHODS OF ANALYSIS

The analytical techniques used by individual laboratories in this study are briefly described below and outlined in the flow diagram (Appendix B). In view of the widespread presence of asbestos, all laboratories

ran blank samples through their entire analytical procedure and took precautions to keep contamination at a minimum level.

Canada Centre for Inland Waters (C.C.I.W.)[1]

A known aliquot of the sample is transferred to a 250 ml plastic bottle and centrifuged for a period of one hour at 30,000 g using a centrifuge with an angular head. The supernatant liquid is decanted and the residue re-suspended in 1 ml of water. A one microlitre aliquot is transferred onto a carbon coated grid, 3 mm in diameter, and dried with the droplet facing downward. The area covered by the residue is estimated on the basis of the results of past droplet area measurements. The grid is examined by means of a transmission electron microscope (TEM) and the number of fibres counted for a minimum of 50 grid squares. Fibres are identified by their morphology and electron diffraction patterns. A filtration step is not employed in this method.

McMaster University[2]

A known aliquot of the sample is filtered through a 0.4 um pore size nuclepore filter. The filter is placed in a clean vial, a measured amount of fibre-free water is added and the fibres are dislodged by ultrasonic vibration at 10-30 KHz. One to five microlitre aliquots are transferred to carbon coated grids, 3 mm in diameter, which had been previously treated with a wetting agent. The grids are dried under an infrared lamp with the drops facing downward. At least two grids are prepared for each sample, and these examined using a TEM. For each grid, either the number of fibres

in ten grid squares, or a total of approximately 100 fibres, is counted, whichever comes first. In selected instances, energy dispersive X-ray fluorescence is used for semi-quantitative chemical analysis. The lengths and widths of the fibres are also measured. The data are processed through a computer.

Ontario Research Foundation (O.R.F.)[3]

A known aliquot of the sample is filtered through a 0.1 um pore size nuclepore or millipore filter. The filter is placed in a clean vial and ashed at a low temperature in an oxygen plasma furnace to destroy the organic matter. The sample is re-suspended in double distilled water by ultrasonification and centrifuged onto a glass cover slip in a special tube that has a removable bottom. The cover slip is removed, dried and coated with carbon. The coated layer is scored, divided into segments, approximately three square millimetres in area, removed by floating onto the surface of water and one of the segments is picked up on a microscope grid. The samples are viewed with the aid of a TEM, and fibres on ten grid squares are counted and identified by their morphology and characteristic electron diffraction patterns. The fibres' lengths and widths are also measured. Results are calculated by a computer using a program developed for the purpose.

FACTORS AFFECTING ANALYTICAL RESULTS

In a report published by the Great Lakes Research Advisory Board[4], twenty-four points have been enumerated as potential causes of error, including manner of sampling, conditions of storage, preparative procedures, enumeration techniques, contamination and failure to see and to identify fibres. As reliable standards of known concentrations

of various types of mineral fibres are not currently available, the effects of these factors could not be evaluated by sample spiking or recovery studies. Furthermore, the present methods used in the determination of asbestiform mineral fibre concentrations in environmental samples also involve some degree of subjectivity on the part of the analyst. For example, the results obtained are dependent on the preferred definition of what constitutes a fibre, criteria used for characterization of fibre type, and electron microscope grid counting techniques.

In this study, two of the participating laboratories supplied definitions and identification criteria for asbestiform fibres. According to McMaster University, an asbestiform particle is taken to be any mineral that has a length to width aspect of 3/1 or greater and occurs in micron and submicron size. There are about 40 minerals that can fit this description.

The O.R.F. also uses the 3/1 aspect ratio as one of the criteria for asbestiform fibre identification. In addition, to be characterized as an amphibole, the fibre must display the correct electron attenuation, have some parallel cleavages and the selected area diffraction pattern must show the typical single crystal fibrous pattern, with the correct layer spacings in the correct orientation relative to the longer dimension of the particle. Chrysotile particles must have the correct electron attenuation, must display characteristic tubular morphology of approximately 40 nm in diameter per fibril and where obtainable, the characteristic diffraction pattern. Generally, the morphology is considered adequate for the identification of chrysotile fibres.

Electron diffraction patterns are very important criteria for fibre identification. However, the electron diffraction pattern produced depends on the orientation of the individual fibre with respect to the electron beam. Since this orientation cannot be precisely determined, the interpretation of the patterns is, also, to some extent, dependent upon the judgement and experience of the analyst.

SUMMARY OF REPORTS FROM PARTICIPATING LABORATORIES

Results obtained from this study were presented by the three laboratories in separate reports covering the first and second sampling phases. The contents of the reports are summarized below.

Canada Centre for Inland Waters

The results obtained from the two sample sets are presented in Table 1.

TABLE 1

Asbestiform fibre concentration
(millions of fibres per litre)

First sample set	Second sample set
0.2	0.2
0.6	0.6
0.9	0.7
1.0	0.8

It is significant that this laboratory found chrysotile to be the only asbestiform type fibre present in the samples. The median length of the fibres counted was found to be 0.5 um in both sets of samples. No particle size distribution data were submitted. In a personal communication, the C.C.I.W. analyst has raised the point that because of the small number of fibres counted, a particle size distribution analysis would be of little value.

McMaster University

The results obtained from the analysis of the samples are presented in Table 2.

TABLE 2

Asbestiform fibre concentration*
(millions of fibres per litre)

First sample set	Second sample set
6.5	3.4
6.8	3.7
8.7	4.0
29.0	5.5

* Nuclepore filters.

In the first sample set, 5 of 24 asbestiform fibres analyzed by X-ray fluorescence were found to be cummingtonite; the same number were amphiboles, excluding commingtonite, and the remainder were classified as "unknown"** No chrysotile fibres were detected.

For the second set of samples, the total counts for the grids examined were: 132 amphibole fibres, 83 "unknown" fibres and 79 chrysotile fibres. An X-ray examination of 15 fibres showed 7 of them to be amphiboles, and the remainder "unknown" asbestiform fibres. During the analysis of the second sample set, it was found that the nuclepore filters were contaminated with chrysotile fibres. Although the chrysotile fibres counted were reported, it was recommended that little weight be given to this portion of the results from the second set, and that only amphibole and "unknown" fibres should be considered for comparative purposes. In Table 2, therefore, the fibre counts given for the second

** any unidentifiable asbestiform fibre

sample set do not include those obtained for chrysotile.

The detailed mineralogical study of the fibres was carried out using energy dispersive X-ray analysis. Union Internationale Contre Le Cancer asbestiform minerals were used as reference standards. Results from this analysis are presented in Appendix C.

The means and ranges of values for fibre length, width, mass and aspect ratio are given in Table 3.

TABLE 3

Fibre dimensions

Fibre type		First sample set		Second sample set	
		Mean*	Range	Mean*	Range
Amphibole and "unknown"	Length (um)	1.05	0.4-8.40	0.91	0.40-3.0
	Width (um)	0.20	0.04-0.35	0.13	0.04-0.35
	Aspect ratio $\frac{\text{length}}{\text{width}}$	5.2	2.0-70.0	6.8	2.0-40.0
	Mass (ug/l)				
	amphibole	2.5	1.3-5.8	0.8	0.63-1.0
	"unknown"	3.6	1.8-8.2	0.5	0.39-0.65
Chrysotile	None detected			Chrysotile excluded, see text.	

* Calculated by the Ministry of the Environment

Ontario Research Foundation

The results obtained from the analysis of the samples are presented in Table 4.

TABLE 4

Asbestiform fibre concentration*
(millions of fibres per litre)

First sample set	Second sample set
0.01	BDL**
0.08	BDL
0.13	BDL
0.16	0.04

* Samples filtered through nuclepore filters.
** Below detection limit.

Aliquots of the water samples were filtered through both nuclepore and millipore filters. The level of asbestos contamination (chrysotile) was higher in millipore than in nuclepore filters, and it was suggested by the analyst that only results from the analysis of the nuclepore-filtered samples be considered for comparison of fibre counts with those of the other laboratories.

The fibres observed were classified as amphibole or chrysotile. Other fibrous material present was not counted. The concentrations found for the 2 fibre types, after sample filtration using nuclepore filters are given in Table 5.

TABLE 5

Amphibole and Chrysotile fibre concentration
(millions of fibres per litre)

First sample set		Second sample set	
Amphibole	Chrysotile	Amphibole	Chrysotile
0.01	BDL (<0.01)	BDL (<0.02)	BDL (<0.02)
0.03	0.05	BDL (<0.02)	BDL (<0.02)
0.04	0.09	BDL (<0.02)	BDL (<0.02)
0.07	0.09	BDL (<0.02)	0.04

The means and ranges of values for fibre length, width, mass and aspect ratio are given in Table 6.

TABLE 6

Fibre dimensions

Fibre type		First sample set		Second sample set	
		Mean*	Range	Mean	Range
Amphibole	Length (um)	0.99	0.49-2.24	None detected	
	Width (um)	0.29	0.13-0.58		
	Aspect ratio	3.4	1.1-16.7		
	Mass (ug/l)	0.0136	0.0105-0.0181		
Chrysotile	Length (um)	0.59	0.36-1.57	Insufficient data for evaluation	
	Width (um)	0.049	0.045-0.089		
	Aspect ratio length/width	13.1	7.5-35.0		
	Mass (ug/l)	0.000155	BDL - 0.000237		

* Calculated by the Ministry of the Environment

An alternate technique was employed by the Ontario Research Foundation to corroborate the finding that the amphibole concentration in the samples did not exceed that of chrysotile. The technique consisted of sample filtration onto a nuclepore filter, drying, carbon film coating and fibre counting, and identification by means of a scanning electron microscope (SEM), equipped with an energy dispersive X-ray analyzer. By this method, particles 1 um in length and larger can be identified. From other work performed by the Foundation, it was established that approximately 33 per cent of amphibole fibres from Lake Superior fall into this size category. One sample from the first set was analyzed using the SEM, and the amphibole fibre count obtained was multiplied by the appropriate factor. The product was of the same order of magnitude as the previous TEM fibre count, and thus confirmed the reported TEM value for the same sample. In addition, it was shown that the amphibole fibres were mainly hornblende, and that no cummingtonite was present.

BACKGROUND DETERMINATION AND MINIMUM DETECTION LIMIT

There is always a risk that samples will become contaminated, especially by chrysotile, during sampling and analytical procedures. C.C.I.W. (1) has published information on chrysotile fibre contamination of carbon-coated electron microscope grids. By chemical and ultrasonic cleaning of glassware used in the analyses, the mean fibre background could be maintained at a level of less than 1 fibre per 10 grid squares, i.e., less than 0.1 million fibres per litre, assuming that a 250 ml water sample is processed. The detection limit was defined by C.C.I.W. as twice the mean fibre background.

McMaster University and O.R.F. also found on occasion contamination of nuclepore filters used in sample filtration. McMaster University reported that the paper discs separating individual nuclepore filters in packaging, contained chrysotile fibres, resulting in a varying degree of contamination of the nuclepore filters. By running blank distilled water samples through the entire analytical procedure, McMaster University measured the mean fibre background of chrysotile to be 0.1 fibre per grid square, i.e. approximately 0.1 million fibres per litre, assuming a 500 ml water sample was processed. The detection limit was defined as twice the mean fibre background. O.R.F.[5] has published data on background asbestiform fibre levels in nuclepore, millipore and delbag filters. For 47 mm nuclepore filters, the levels are (3300 ± 870) for chrysotile and (570 ± 430) for amphibole fibres per filter. The detection limit was defined as 1 fibre per 10 grid squares, i.e. approximately 0.01 million fibres per litre, assuming a 200 ml water sample was processed.

SUMMARY OF RESULTS AND DISCUSSION

It was noted in the first set of samples, that, together with the asbestiform fibres, a few black-coloured particles and a large amount of material such as diatoms, organic matter and minerals were observed to be present. Subsequently, O.R.F. analyzed the black particles and found them to contain iron, calcium, silicon and some manganese. The particles were assumed to have resulted from corrosion of the iron piping in the water supply system. The extraneous particulate matter, however, did not interfere with the analysis of the asbestiform fibres.

The results from the analysis of both sets of water samples are shown in Table 7.

TABLE 7

Asbestiform fibre concentration
(millions of fibres per litre)

Laboratory		C.C.I.W.				McMaster University				O.R.F.			
Sample set		First		Second		First		Second		First		Second	
Container number		2	4	12	14	3	7	10	11	5	6	9	13
Fibre concentration	A*	0.2	0.6	0.6	0.2	29	6.5	3.4	3.7	0.13	0.08	BDL	BDL
	B*	0.9	1.0	0.7	0.8	6.8	8.7	5.5	4.0	0.16	0.01	0.04	BDL
** Mean for each sample set		0.68		0.58		12.75		4.15		0.10		0.01	
** Mean for both sample sets		0.63				8.45				0.06			

* A and B are duplicate samples.
** Arithmetic means

As can be seen from the table, the total asbestiform mineral fibre counts, in millions of fibres per litre, ranged from 0.01 to 29 for the first sample set and from below detection limit to 5.5 for the second set. The agreement in results within each laboratory for the randomly distributed samples suggests that all the water samples of each set were essentially identical. The precision of the analytical results for any one laboratory is considered to be satisfactory (approximately 1 order of magnitude).

The means of the asbestiform fibre concentration levels, calculated for each laboratory, in millions of fibres per litre (Table 7), vary from 0.10 to 12.75 for the first sample set and from 0.01 to 4.15 for the second set. The apparent reduction in the fibre concentration in the second sample set may be attributed to the influence of the prevailing wind direction at the time of sampling.

The means of the asbestiform fibre concentration levels were also calculated for each laboratory for the combined sets. These means, 0.63, 8.45 and 0.06 million fibres per litre for C.C.I.W., McMaster University and O.R.F. respectively, are seen to differ by approximately 1 or 2 orders of magnitude.

The results submitted by the laboratories, besides differing in total fibre counts, also differed with respect to the type of fibre, and the number and mass of each type found in the samples.

C.C.I.W. found only chrysotile in both sample sets. McMaster University, in the first sample set, found amphiboles, including cummingtonite, at a mean level of 5.3 million fibres per litre and "unknown" fibre types at a mean level of 7.45 million fibres per litre. In the second sample set a mean of 2.54 million fibres per litre of amphiboles and a mean of 1.61 million fibres per litre of "unknown" fibre types were found. O.R.F. reported chrysotile and amphibole fibres to be present in the first sample set, in mean amounts of 0.06 and 0.04 million fibres per litre respectively. In the second sample set, essentially no fibres were detected.

The values for fibre dimensions (length and width), measured by the laboratories, are in good agreement. C.C.I.W. gave the median length of chrysotile as 0.5 um for both sets of samples. The mean dimensions for amphiboles and "unknown" fibres, calculated from McMaster University data, were 1 um in length and 0.20 um in width for the first sample set, and 0.9 um in

length and 0.1 um in width for the second sample set. O.R.F. mean values for the first sample set for chrysotile fibres were 0.6 um in length and 0.05 um in width, and for amphiboles, 1.0 um in length and 0.30 um in width. These observations suggest that sample preparation techniques did not cause a breakdown of the chrysotile and amphibole fibres, and that the differences in the fibre counts obtained were due to other causes.

The amphibole mean fibre mass concentrations can be compared, for the first sample set, for McMaster University and O.R.F. The difference is seen to be 2 orders of magnitude (Tables 3 and 6). This is to be expected, because of the agreement between the 2 laboratories as to fibre dimensions.

Although it is possible to derive a single overall geometric or arithmetic mean figure (0.49 or 3.03 million fibres per litre, respectively), for the 24 samples analyzed by the laboratories, it is apparent that such a figure would not be meaningful, for, as discussed above, it would be based on evaluations of different asbestiform fibre types. The means, calculated from the analytical data for each of the three laboratories, for the combined sample sets, are considered to be indicative of the range of values within which the actual concentration of asbestiform fibres may lie.

The between-laboratory differences discussed above may be due to various factors. One of the factors, the effect of which constitutes part of this study, is the counting technique employed by the individual laboratories.

GRID EXCHANGE EXPERIMENT

To investigate the effect of the counting technique, an electron-microscope grid exchange experiment was carried out by McMaster University and O.R.F.

Two grids, prepared and analyzed by O.R.F. from the first water sample set, were submitted to McMaster University for re-counting. Likewise, two grids were re-prepared from the second sample set, and analyzed by McMaster University, and submitted to O.R.F. for re-counting. Each laboratory used the same counting technique as previously employed in analyzing the water samples.

TABLE 8

Grid exchange data
(fibres per grid square)

Grids prepared by McMaster University					Grids prepared by O.R.F.				
Grid No.	Analyzed by				Grid No.	Analyzed by			
	McMaster University		O.R.F.			McMaster University		O.R.F.	
1	1.68	A	0.2	A	3	0.16	A	0.30	A
	-	C	1.5	C		N.D.	C	0.40	C
	1.12	O	-	O		N.D.	O	-	O
2	1.62	A	0.25	A	4	0.3	A	0.10	A
	-	C	12.0	C		0.14	C	N.D.	C
	1.08	O	-	O		0.4	O	-	O

A = amphibole
C = chrysotile
O = "other"
- = not reported
N.D. = none detected

From Table 8, it is seen that the fibre counts obtained by the two laboratories differ for any given grid. For chrysotile, the results from 2 grids only are given for each laboratory. No comparison can be made because some of the results are below detection limit and the chrysotile fibre counts presented in grid 1 and 2 suggest that chrysotile contamination occurred during preparative procedures.

For the other fibres, O.R.F. counted amphibole fibres and McMaster University counted "unknown" asbestiform fibres in addition to amphibole fibres. The difference in the mean counts of the total fibres, excluding chrysotile, is approximately 1 order of magnitude for the same grid counted by the two laboratories. This difference in results is mainly due to the difference in the fibre counting techniques and identification criteria used by the laboratories.

Hence, it is concluded from the grid exchange experiment that the difference of approximately 1 order of magnitude in the inter-laboratory analytical results may be attributed to the different fibre counting techniques and identification criteria used by the two laboratories.

RESULTS OF OTHER STUDIES AND SURVEYS

Both Canadian and United States Governmental agenices have conducted studies on the levels of asbestiform fibres in water supplies.

TABLE 9

Asbestos fibre count
(distribution system - water)

Sample location	Source	Fibre count in millions per litre	Estimated mass concentration, ug/l
Toronto	L. Ontario	1.90	0.000941
Belleville	Bay of Quinte	0.533	0.000937
Brantford	Grand River	0.570	0.00113
Brockville*	St. Lawrence R.	0.446	0.000602
Chatham	Thames River	0.595	0.00157
Cornwall	St. Lawrence R.	2.11	0.000729
Hamilton	L. Ontario	0.694	0.000154
London	L. Huron	0.456	0.000429
Niagara Falls	Niagara R.	2.58	0.00225
North Bay*	Trout L.	0.384	0.000104
Oshawa	L. Ontario	0.557	0.000159
Ottawa	Ottawa R.	0.136	0.000093
Pembroke*	Ottawa R.	2.85	0.000538
Peterborough	Ottonabee R.	1.86	0.00354
Port Colborne	Welland Ship Canal	0.608	0.000847
Sarnia*	L. Huron	3.87	0.00213
Sault Ste. Marie*	St. Mary's R.	0.248	0.000141
St. Catherines	Welland Ship Canal	1.03	0.00156
Sudbury*	Ramsay Lake	0.297	0.000542
St. Thomas	L. Erie	1.60	0.000500
Thunder Bay*	L. Superior	0.830	0.000235
Welland	Welland Ship Canal	0.820	0.000479

NOTE: *means No Filtration Plant

Cunningham and Pontefract[6] published data on the fibre content of tap water samples from various localities. Examples of results reported, as mainly chrysotile, in millions of fibres per litre, are 2.0, 2.4, and 4.4 for Ottawa, Montreal and Toronto respectively (filtered water supplies), 9.5 for Hull and 172.7 for a sample from Thetford Mines, Eastern Townships (not filtered). Kay[7] published fibre concentrations, as mainly chrysotile, determined in samples from 22 municipal water supplies in Ontario. The values ranged from 0.136 to 3.87 million fibres per litre (Table 9). Anderson[8] of the United States Environmental Protection Agency reported the amphibole average fibre levels in 5 water supplies from the western Lake Superior region to range from 0.4 to 63.1 million fibres per litre. The concentrations of total asbestiform fibres found in the present study, agree generally with the chrysotile or amphibole levels found in the other studies.

Anderson[8] also reported the findings of an inter-laboratory study. Seven laboratories, following their own procedures, analyzed aliquots of 5 water samples and a standard amphibole fibre suspension. In addition, 5 aliquots of an aqueous suspension of amphibole fibres were filtered, and segments of the filters were analyzed by two laboratories. The findings are also in agreement with those of the present study, i.e., for fibre counts of the same sample, the reproducibility within any one laboratory is acceptable and within an order of magnitude, but the discrepancy between laboratories can be as high as 2 orders of magnitude.

CONCLUSIONS

The arithmetic means and ranges of the analytical results obtained by each of the three laboratories, for both sample sets, in millions of fibres per litre, are as follows:

	Mean	Range
C.C.I.W.	0.63	0.2 - 1.0
McMaster University	8.45	3.4 - 29
O.R.F.	0.06	BDL - 0.16

It can be seen that there is a wide spread, of approximately 2 orders of magnitude, between the highest and lowest mean fibre concentrations.

The three laboratories also reported different fibre types, and different numbers and masses of each type, to be present in the samples. C.C.I.W. found only chrysotile to be present, McMaster University, chrysotile, amphiboles and "other" types, and O.R.F. chrysotile and amphiboles.

As there is no evidence to suggest that any laboratory is more correct in its methodology or definition of fibre type than any other, the means of the analytical data, for both sample sets, must be presented separately for each laboratory. These arithmetic means, given above, are indicative of the range of values within which the actual concentration of asbestiform fibres in the Thunder Bay water supply may lie.

An examination of the within-laboratory analytical results, taking into account the initial random distribution of the samples to the laboratories, indicates that all the samples comprising each set were essentially identical.

There is a slight difference in the asbestiform fibre levels found in the first and second sample sets. The difference may be attributable to the effect of the prevailing wind direction on the fibre concentrations.

The precision of the analyses performed by any one laboratory, recognizing the number of factors which may influence the results, was satisfactory, and was, as expected, better for relatively high values than for low ones.

It is noted that results which have been presented by other investigators who have carried out inter-laboratory studies and analyses of asbestiform fibres in water supplies have shown similar variations to those obtained in the present study.

From the limited experiments involving electron microscope grid exchanges and re-counts carried out by McMaster University and O.R.F., together with data from the individual laboratory sample analyses, it is concluded that an approximately 1 order of magnitude difference, in the average results between laboratories, may be attributed to differences in counting techniques, including asbestiform mineral identification criteria.

RECOMMENDATIONS

Large discrepancies occur in the analytical results reported by the laboratories participating in this study. These discrepancies reflect the present state of the art in the determination of asbestiform fibre levels in water, and lead to difficulties in attempting to reconcile the findings.

In view of these shortcomings, it is recommended that the leading laboratories presently engaged in asbestiform analysis should establish a committee charged with the following responsibilities:

(1) To provide a standard definition as to what constitutes an asbestiform mineral fibre.

(2) To develop approved methods for the determination of asbestiform fibres in environmental samples.

(3) To develop guidelines regarding acceptable requirements for precision and accuracy.

(4) To develop quality control and data validation procedures.

Pending a more complete resolution of the analytical and identification problems in asbestiform fibre determination, it is recommended that caution should be exercised with regard to directly comparing the results obtained by any one laboratory with those of another.

APPENDIX A

GUIDELINES FOR AN INTER-LABORATORY STUDY

INTRODUCTION

The mining and processing of asbestos, together with its widespread use in the fabrication of many products, has led to serious concern about its present levels and distribution throughout the environment. The concentration of asbestos in ambient air, food, water, is not well known and analytical methods to determine it in various substrates are not yet standardized. The health hazards caused by asbestos are still a matter of speculation, although it is suspected of producing lung cancer in humans.

The Ontario Ministry of the Environment has several programs presently underway to obtain knowledge about the levels of asbestos in the environment. In the field of air pollution, surveys are being undertaken to determine the asbestos concentration in ambient air. Some water quality surveys have also been conducted and others are planned. In view of the questions currently raised ab out the asbestos content of the drinking water in Thunder Bay, the Laboratory Services Branch is conducting an inter-laboratory study of this problem.

The following guidelines are suggested:

(a) to determine the asbestiform fibre concentration of the Thunder Bay water supply;

(b) to ascertain the range of values obtainable from the analysis of identical samples by the participating laboratories;

(c) to comment on the probable cause of variabilities in results within and between laboratories.

It is expected that the experimental design and the results will help to determine the level of the asbestos fibre concentration and to answer questions frequently put by the medical and legal professions regarding the validity of the results, i.e. the confidence that can be placed on the data supplied by the analyst.

The following laboratories have agreed to participate in this study:

(1) Canada Centre for Inland Waters

(2) McMaster University

(3) Ontario Research Foundation

EXPERIMENTAL DESIGN

This experiment takes into account the following factors which may affect the results of the fibre analysis:

(1) Sampling error

(2) Error in dividing samples

(3) Wind directions - off-shore and on-shore

(4) Methodology

(5) Expertise in identifying asbestos in water

SAMPLING

Prior to final sample collection, each containing vessel shall be vigorously rinsed with an appropriate amount of water from the corresponding source. The following sampling scheme is suggested:

(1) Eight (8) 10-litre samples are to be collected during an on-shore wind

(2) Eight (8) 10-litre samples are to be collected during an off-shore wind

(3) Two (2) 1-litre duplicates are to be taken from each of the original sixteen samples

(4) Of the 32 samples, 8 are to be sent to each laboratory.

The samples will be collected at the intake to the water distribution system.

It is expected that the first set of samples will be collected on May 5th, 1975, by Northwestern Regional and Laboratory personnel.

ANALYSIS

Each laboratory will analyze 8 samples by electron microscopy and include in the reports of their results the following for each type of fibre (chrysotile, amphibole):

(1) the number of fibres per litre of water

(2) concentration in weight per litre of water

(3) the length, width and aspect ratio

(4) size distribution pattern

(5) one photograph of each type of fibre with its electron diffraction pattern and X-ray spectrum if feasible.

The participating laboratories shall further provide the following details of the analytical procedure with regards to:

(a) sample preparation, aliquot used, treatment, etc.

(b) number of grids squares counted

(c) the method of sizing

(d) method of calculating results

Each set of samples is to be processed on the same day by all laboratories and analyzed microscopically as soon as possible. It is understood that the same operator in each laboratory will be responsible for the analysis of all the samples.

ANALYSIS OF THE DATA

The scheme for distribution of samples was selected from a computer print-out of random numbers and the expected results from the three laboratories are summarized in the following table:

Lab No.	1		2		3	
Wind	C	D	C	D	C	D
sample randomly distributed	2 4	12 14	3 7	10 11	5 6	9 13
A B						

C and D represent on or off-shore winds depending on the wind direction at the time of first sampling.

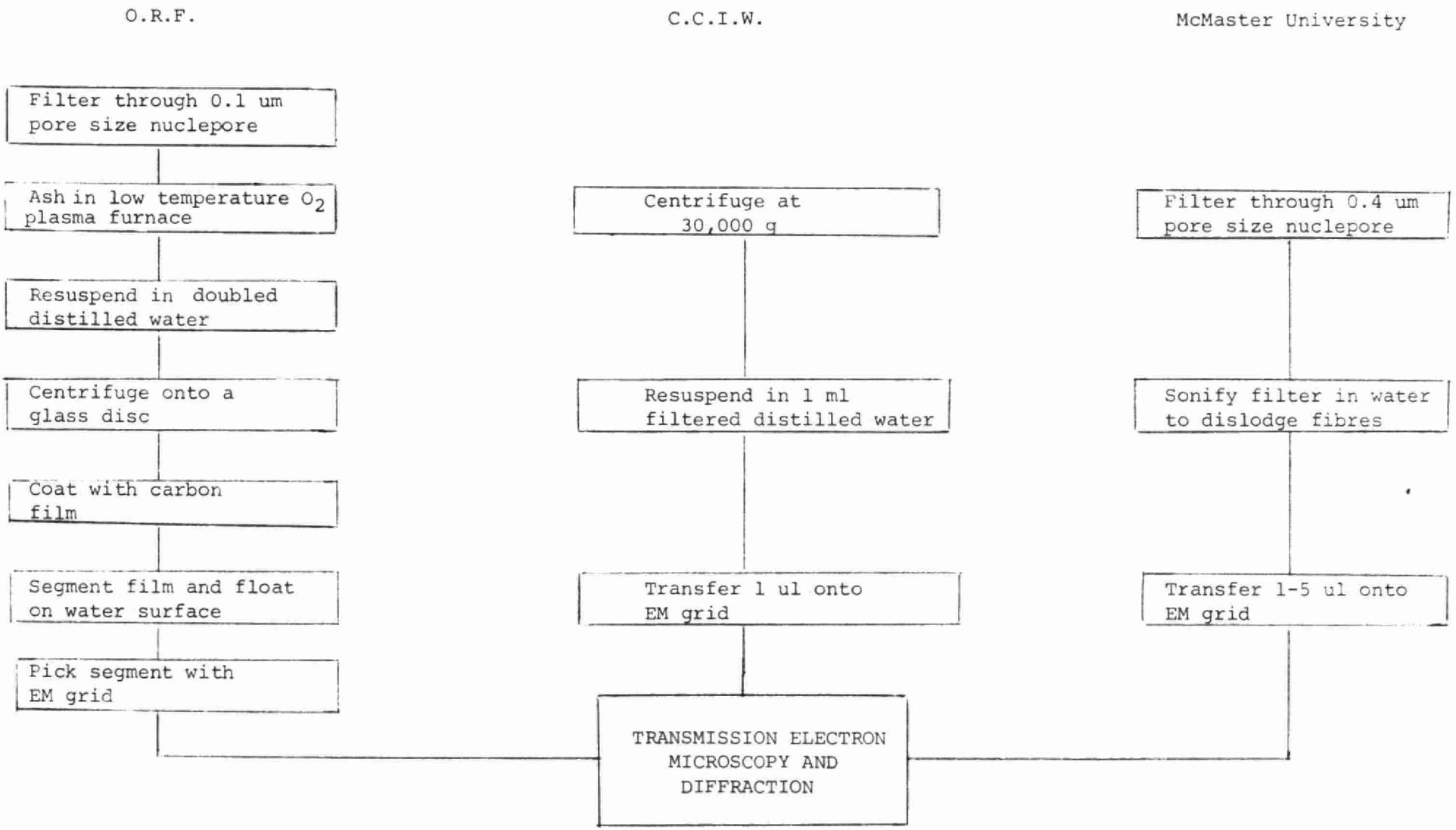
By using the analysis of variance we would be able to determine the concentrations of chrysotile and amphibole fibres in Thunder Bay city drinking water measured by the three laboratories with respect to the climatic conditions, sampling error, error in fibre estimation and sample preparation and duplication of samples.

The Laboratory Services Branch will undertake the statistical analysis of the data, its interpretation and the preparation of the report.

Laboratory Services Branch
Ontario Ministry of the
Environment

A P P E N D I X B

METHODS OF ASBESTIFORM MINERAL FIBRE ANALYSIS



APPENDIX C

TABLE 10 ELEMENTAL ANALYSIS BY XRF ON TEM OF INDIVIDUAL FIBRES BY McMASTER UNIVERSITY

(Values are percent intensities corrected for background)

UICC STANDARDS

NAME	Si	Al	Fe	Mg	Na
Canadian Chrysotile	56-61	--	0-1	38-45	--
Amosite (cummingtonite)	41-47	0-1	46-52	3-5	0-1
Crocidolite	45-55	--	43-54	0-1	1-2
Anthophyllite	66-73	--	3-10	23-28	--

APPENDIX C continued

F I R S T S A M P L E S E T

Fibre	Fibre (um) length/width	Si	Al	Fe	Mg	Ca	Na	K	Mn	S	Cr	Probable Mineral
1	1.0/0.2	43	5	31	3	1	4			1	9	Amphibole
2	1.0/0.2	55	4	36			1	3				Amphibole or feldspar
3	2.6/0.3	52		46							2	Cummingtonite
4	5.0/0.2	51		48			1					?
5	2.0/0.6	45	2	33	7	8					1	Actinolite-tremolite
6a	3.5/0.2	49	1	43	1		2				1)	
same, different spot		55	1	42							1)	Cummingtonite
7	8.0/0.15	45		55								Cummingtonite
8	4.0/0.3	51		48			1					Cummingtonite
9	24/0.3	94	3	1				2				Diatom Fragment
10	1.2/0.1	66		34								Cummingtonite
11	3.8/0.2	51		48			1					Amphibole
12	1.4/0.1	44		31	1	10					2	Actinolite-tremolite
13	1.4/0.1	63	8		1	26						Wollastonite? Amphibole?
14	1.0/0.1	51	2	35						3	8	Amphibole
15	2.8/0.8			79			1				20	Ilmenite-magnetite
16	7.0/0.2	83	6				3	5		Tr		Feldspar
17	1.2/0.1	91	1					6	1			Diatom
18	2.0/0.2	68	6				5	3		15		Feldspar Cr?
19	2.4/0.2	61	10		1	26						Plagioclase? Prehnite?
20	2.0/0.2	77	5			2	2	10			1	Coated Diatom?
21	1.8/0.1	79				1	2	12			4	Coated Diatom?
22	4.5/0.2	67	2				12	14		1	2	Feldspar?
23	1.2/.15	75	5	10				8				Coated Diatom?
24	1.2/.1	69	3			1	7	12			6	Coated Diatom?

APPENDIX C continued

SECOND SAMPLE SET

Fibre	Fibre length/width	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn	Ni	P	S	Cr	Probable Mineral
1	2/.04	19	Tr	1		4	56	2		Tr	3		9	2	?
2	0.8/.07	97				2						1			?
3	1.5/0.1	74	3		1	7	Tr					2	11	Tr	diatom + ?
4	4.5/0.2	82	6			3	1	3				2	1		diatom
5a	2.0/.15	60	4	Tr		1	4	2				1	3	22	feldspar?
5b		71	5			10	2	5				1	4		feldspar?
6	2.7/.15	75	3			6	2	4				1	5	Tr	stilbite? mordenite?
7	.7/.1	27	1	33		3	7	4					13	11	grunerite
8	1.5/.1	52		46								Tr		Tr	grunerite
9	.8/.1	88	2		Tr	5	1	1				1			stilbite? mordenite?
10	1/.1	57	1	15	23	1						1			cummingtonite?
11	.7/.15	61	1	2	18	16						1		Tr	tremolite
12	.8/.05	47	3	34	Tr	7		11		3		1	Tr	1	amphibole (actinolite?)
13	.7/.05	59	35				4	1				Tr		Tr	plagioclase
14	1.3/.05	53	Tr	34		1		6			Tr	Tr	1	3	cummingtonite
15	.6/.05	53	8	21	4	11						Tr		1	actinolite - tremolite
16	.9/.05	8				Tr			92						rutile
17	1/.05	57	7	1	2	20	9	1					Tr		hornblende?

Tr = Trace amount

REFERENCES

1. R. W. Durham, T. W. S. Pang, "Asbestos Fibres in Lake Superior". Presented at the C.I.C.-C.C.I.W. Symposium on Water Quality Parameters, November, 1973.

2. J. R. Kramer, O. Mudroch, S. Tibor, "Asbestos in the Environment". For the I.J.C. Great Lakes Research Advisory Board, May, 1974.

3. E. J. Chatfield, "Quantitative Analysis of Asbestos Minerals in Air and Water". 32nd Ann. Proc. Elect. Micro. Sco. Amer., St. Louis, Missouri, 1974.

4. M. P. Bratzel, et al, "Asbestos in the Great Lake Basin with emphasis on Lake Superior". A report to the I.J.C. from the Great Lakes Research Advisory Board. February, 1975.

5. E. J. Chatfield, "Asbestos Background Levels in Three Filter Media used in Environmental Monitoring". 33rd Ann. Proc. Elect. Micro. Sco. Amer., Las Vegas, Nevada. August, 1975.

6. H. M. Cunningham, R. Pontefract, "Asbestos Fibres in Beverages and Drinking Water". Nature, Vol. 232, pp. 332-333, 1971.

7. G. Kay, "Ontario Intensifies Search for Asbestos in Drinking Water". J. Water and Pollution Control, pp. 33-35, September, 1973.

8. C. H. Anderson, "Current Capacity and Needs in Particle and Identification Variance in Analysis by Several Laboratories". Presented at the Amer. Waste Water Assoc. Meeting, Minneapolis, Minnesota, 1975.